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Electromotive force, emf (cells)

by

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The voltage or electric potential difference across the terminals of a cell when no current is drawn from it. The emf of a cell is the sum of the electric potential differences (PDs) produced by a separation of charges (electrons or ions) that can occur at each phase boundary (or interface) in the cell. The magnitude of each PD depends on the chemical nature of the two contacting phases. Thus, at the interface between two different metals, some electrons will have moved from the metal with a higher free energy of electrons to the metal with a lower free energy of electrons. The resultant charge separation will produce a PD (just as charge separation produces a voltage across a capacitor) that, at equilibrium, exactly opposes further electron flow. Similarly, PDs can be produced when electrons partition across a metal|solution interface or metal|solid interface, and when ions partition across a solution|membrane|solution interface.

The origin of emf: the Daniell cell as an example.

We can see how a cell emf is composed of the sum of interfacial PDs by considering the historic Daniell cell shown in Fig. 1. This can be schematically represented by:

$$\mathrm{Cu}' \underset{a}{|} \mathrm{Zn} \underset{b}{|} \text{aq soln(1): } \mathrm{ZnSO_4} \underset{c}{\vdots} \text{aq soln(2): } \mathrm{CuSO_4} \underset{d}{|} \mathrm{Cu} \qquad \text{Schem}$$

where a solid line indicates a phase boundary and the dashed line a porous barrier permeable to all the ions in the adjacent solutions. The barrier prevents physical mixing of the $ZnSO_4$ and $CuSO_4$ solutions.

The cell emf is the open-circuit (i.e., zero current) potential difference measured between the two Cu leads (any potential-measuring device must ultimately measure the potential difference between two chemically identical phases). We can write an expression for the cell emf in terms of the electrochemical potentials of the species involved in the interfacial equilibria. The electrochemical potential $\tilde{\mu}_j^{\alpha}$ of species j in phase α is defined by:

$$\tilde{\mu}_j^{\alpha} = \mu_j^{\alpha} + z_j F \phi^{\alpha} \tag{2}$$

where μ_j^{α} is the chemical potential of species j in phase α, z_j is the charge (with sign) on the species, F is Faraday's constant (96497 C for Avogadro's number of electrons), and ϕ^{α} is the inner potential of phase α. The term $z_j F \phi^{\alpha}$ in eq 2 is the electrical work required to move $z_j F$ coulombs of charge into phase α from a vacuum at infinite distance. For a species in solution eq 2 can be written:

$$\tilde{\mu}_j^{\alpha} = \mu_j^{o\alpha} + RT \ln a_j^{\alpha} + z_j F \phi^{\alpha} \tag{3}$$

where $\mu_j^{o\alpha}$ is the standard chemical potential of species j in phase α, R is the gas constant (8.3144 Joules/mole/degree), T is the temperature in degrees Kelvin, and a_j^{α} is the activity of species j in phase α. For a neutral species (i.e., when $z_j = 0$),

$$\tilde{\mu}_j^{\alpha} = \mu_j^{\alpha} = \mu_j^{o\alpha} + RT \ln a_j^{\alpha} \tag{4}$$

For a fully ionized solution species at low concentrations, a_j^{α} is well approximated by the concentration c_j^{α}; the activity of a pure phase (e.g., zinc and copper in the Daniell cell) is defined as unity.

The value of $\tilde{\mu}_j$ must be identical for any species j equilibrated between two different phases. Thus for equilibrium of species j between phases α and β:

$$\tilde{\mu}_j^{\alpha} = \tilde{\mu}_j^{\beta} \tag{5}$$

More generally one can write for any interfacial equilibrium between phases α and β:

$$\sum_i \nu_j \tilde{\mu}_j^{phase} = 0 \tag{6}$$

where ν_j is the stoichiometric number of species j (ν_j is positive for products and negative for reactants) and $\tilde{\mu}_j^{phase}$ is the electrochemical potential of species j in the phase in which it is located. Thus, for the interfacial equilibrium $Cu^{2+} + 2e^- \rightleftarrows Cu$ at interface d in Scheme 1, eq 6 becomes $\tilde{\mu}_{Cu^{2+}}^{soln(2)} + 2\tilde{\mu}_{e^-}^{Cu} = \tilde{\mu}_{Cu}^{Cu}$.

We now use these equations to quantify the PDs across each of the interfaces in Scheme 1. We will assume that the PD across interface c is zero (a good approximation when the separator is equally permeable to all the ions in the two adjacent phases). For interfaces a, b, and d of Scheme 1 we can write:

interface a (partitioning of electrons between Cu' and Zn phases):

$$\tilde{\mu}_{e^-}^{Cu'} = \tilde{\mu}_{e^-}^{Zn} \tag{7}$$

interface b (equilibrium: $Zn^{2+} + 2e^- \rightleftarrows Zn$):

$$\tilde{\mu}_{Zn^{2+}}^{soln(1)} + 2\tilde{\mu}_{e^-}^{Zn} = \tilde{\mu}_{Zn}^{Zn} \tag{8}$$

interface d (equilibrium: $Cu^{2+} + 2e^- \rightleftarrows Cu$):

$$\tilde{\mu}_{Cu^{2+}}^{soln(2)} + 2\tilde{\mu}_{e^-}^{Cu} = \tilde{\mu}_{Cu}^{Cu} \tag{9}$$

Rearranging eqs 7–9 gives:

$$\tilde{\mu}_{e^-}^{Cu} - \tilde{\mu}_{e^-}^{Cu'} = \tilde{\mu}_{e^-}^{Cu} - \tilde{\mu}_{e^-}^{Zn} = \tfrac{1}{2}\left[\tilde{\mu}_{Cu}^{Cu} - \tilde{\mu}_{Cu^{2+}}^{soln(2)}\right] - \tfrac{1}{2}\left[\tilde{\mu}_{Zn}^{Zn} - \tilde{\mu}_{Zn^{2+}}^{soln(1)}\right] \tag{10}$$

Since $\mu_{e^-}^{o\,Cu} = \mu_{e^-}^{o\,Cu'}$ and for an electron $z_{e^-} = -1$, we can use eq 3 to write

$$\tilde{\mu}_{e^-}^{Cu} - \tilde{\mu}_{e^-}^{Cu'} = -F(\phi^{Cu} - \phi^{Cu'}) \tag{11}$$

The cell potential, E_{cell}, is simply the sum of all the equilibrium interfacial PDs (remembering that we've assumed that $\phi^{soln(2)} - \phi^{soln(1)} = 0$) :

$$E_{cell} = (\phi^{Cu} - \phi^{soln(2)}) + (\phi^{soln(1)} - \phi^{Zn}) + (\phi^{Zn} - \phi^{Cu'}) = (\phi^{Cu} - \phi^{Cu'}) \qquad (12)$$

Combining eqs 3 and 11 – 12 (noting that the copper and zinc ions have a charge of 2+ and that the activity of the metal phases is unity):

$$E_{cell} = (\phi^{Cu} - \phi^{Cu'}) = -\frac{1}{F}\left[\tilde{\mu}_{e^-}^{Cu} - \tilde{\mu}_{e^-}^{Cu'}\right] =$$
$$\frac{1}{2F}\left[\mu_{Cu^{2+}}^{o\,soln(2)} - \mu_{Cu}^{o} + \mu_{Zn}^{o} - \mu_{Zn^{2+}}^{o\,soln(1)}\right] + \frac{RT}{2F}\ln a_{Cu^{2+}}^{soln(2)} - \frac{RT}{2F}\ln a_{Zn^{2+}}^{soln(1)} \qquad (13)$$

where E_{cell} is the potential difference between the two copper leads (Scheme 1) measured at open circuit (i.e., when no current passes through the cell) and is therefore the emf of the cell. Dropping the superscripts denoting the solutions, eq 13 can be rewritten as:

$$E_{cell} = \left[E_{Cu^{2+}|Cu}^{o} + \frac{RT}{2F}\ln a_{Cu^{2+}}\right] - \left[E_{Zn^{2+}|Zn}^{o} + \frac{RT}{2F}\ln a_{Zn^{2+}}\right] \qquad (14)$$

where $E_{Cu^{2+}|Cu}^{o}$ and $E_{Zn^{2+}|Zn}^{o}$ are termed the standard electrode potentials (E^{o}'s) of the copper and zinc half cells. Eq 14 is one example of a Nernst equation, which relates cell emf to the activities of the cell constituents.

{*see* CHEMICAL EQUILIBRIUM; CHEMICAL THERMODYNAMICS; ELECTRODE POTENTIAL; ELECTROMOTIVE FORCE (EMF); THERMODYNAMIC PRINCIPLES}

Half cells, standard electrode potentials and reference electrodes.

It is convenient to describe any electrochemical cell in terms of half cells. A half cell consists of an oxidant (Ox) and reductant (Red) such that: Ox + $ne^- \rightleftarrows$ Red; species Ox and Red are commonly referred to as a redox couple. The Daniell cell, for example, comprises the two half cells: $Cu^{2+} + 2e^- \rightleftarrows Cu$ (redox couple is $Cu^{2+}|Cu$) and $Zn^{2+} + 2e^- \rightleftarrows Zn$ (redox couple is $Zn^{2+}|Zn$) with the half-cell potentials $E_{Cu^{2+}|Cu}$ and $E_{Zn^{2+}|Zn}$, given by

$$E_{Cu^{2+}|Cu} = E^o_{Cu^{2+}|Cu} + \frac{RT}{2F} \ln a_{Cu^{2+}} \tag{15}$$

and

$$E_{Zn^{2+}|Zn} = E^o_{Zn^{2+}|Zn} + \frac{RT}{2F} \ln a_{Zn^{2+}} \tag{16}$$

Such expressions are useful only if the E^o value for each half cell is known. Values of E^o can be assigned to any given half cell by arbitrarily specifying that $E^o_{H^+|H_2}$, the E^o for the standard hydrogen electrode (SHE) half cell, $H^+(aq, a = 1) + e^- \rightleftarrows \frac{1}{2}H_2(g, 1\ atm)$, is zero. The temperature dependence $dE^o_{H^+|H_2}/dT$ is also specified as zero. E^o values vs. the SHE for selected half cells are given in Table 1. In principle, any E^o (and its temperature dependence) can be measured directly vs. the SHE or another half cell whose electrode potential has been determined. Such an electrode is termed a *reference electrode*. The reference electrode is a half-cell designed so that its potential is stable, reproducible, and that it neither contaminates nor is contaminated by the medium in which it is immersed. Two convenient reference electrodes commonly used in aqueous systems are the saturated calomel and the silver|silver chloride electrodes (Table 1).

{ ELECTROCHEMISTRY; REFERENCE ELECTRODE ELECTRODE POTENTIAL}

E^o values and thermodynamics of the overall cell reaction.

The E^o values associated with two half cells comprising a cell provide fundamental thermodynamic information about the chemical reaction between the redox couples of the two half cells. Returning to the example of the Daniell cell and combining eqs 13 and 14 we see that

$$E^{o}_{Cu^{2+}|Cu} - E^{o}_{Zn^{2+}|Zn} = \frac{1}{2F}\left[\mu^{o\ soln(2)}_{Cu^{2+}} - \mu^{o}_{Cu} + \mu^{o}_{Zn} - \mu^{o\ soln(1)}_{Zn^{2+}} \right] \tag{17}$$

The term on the lefthand side is the standard cell emf E^{o}_{cell} (i.e., the value of E_{cell} when all the cell constituents are in their standard states of unit activity), and the bracketed term on the righthand side is $-\Delta G^{o}$, where ΔG^{o} is the standard Gibbs energy change of the cell reaction $Cu^{2+} + Zn \rightleftarrows Cu + Zn^{2+}$. Hence we can write eq 17 as

$$E^{o}_{cell} = -\frac{\Delta G^{o}}{2F} \tag{18}$$

More generally, for the two half-cell reactions $Ox_1 + n_1e^- \rightleftarrows Red_1$ and $Ox_2 + n_2e^- \rightleftarrows Red_2$, E^{o}_{cell} is defined by

$$E^{o}_{cell} = E^{o}_{Ox_1|Red_1} - E^{o}_{Ox_2|Red_2} \tag{19}$$

The cell reaction, which involves the transfer of n_1n_2 electrons, is

$$n_2\,Ox_1 + n_1\,Red_2 \rightleftarrows n_2\,Red_1 + n_1\,Ox_2 \tag{20}$$

and eq 18 takes the general form

$$E^{o}_{cell} = -\frac{\Delta G^{o}}{n_1n_2F} = -\frac{\Delta G^{o}}{nF} \tag{21}$$

where $n = n_1n_2$. If the cell is not in its standard state the relation becomes

$$E_{cell} = -\frac{\Delta G}{nF} \tag{22}$$

Using the general thermodynamic relation $\Delta G^o = -RT\ln K_{eq}$ we can also find the equilibrium constant K_{eq} of the cell reaction from the relation:[1]

$$K_{eq} = \frac{[Ox_2]^{n_1}[Red_1]^{n_2}}{[Ox_1]^{n_2}[Red_2]^{n_1}} = \exp\left[-\frac{\Delta G^o}{RT}\right] = \exp\left[\frac{n_1 n_2 F E^o_{cell}}{RT}\right] \tag{23}$$

{*see* CHEMICAL EQUILIBRIUM; CHEMICAL THERMODYNAMICS; THERMODYNAMIC PRINCIPLES}

Membrane potentials as a source of emf.

When two ionic solutions of different composition are separated by a membrane, a PD can develop across the membrane. The complete cell requires electrical contacts with the solutions on each side of the membrane, accomplished with reference electrodes:

re(lhs) | soln(lhs) | membrane | soln(rhs) | re(rhs)

where re(lhs) and re(rhs) are the reference electrodes in the left and right solutions respectively. The cell emf will be:

$$E_{cell} = E_{re(rhs)} + \phi^{soln(rhs)} - \phi^{soln(lhs)} - E_{re(lhs)} \tag{24}$$

The PD across the membrane, $\phi^{soln(rhs)} - \phi^{soln(lhs)}$, is a function of the membrane properties as well as the composition of the adjacent solutions. The simplest example occurs when only one

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[1] For the special case where $n_2 = n_2 = n$, the cell reaction (eq 20) would be written as $Ox_1 + Red_2 \rightleftarrows Red_1 + Ox_2$ and eq 23 becomes

$$K_{eq} = \frac{[Ox_2][Red_1]}{[Ox_1][Red_2]} = \exp\left[-\frac{\Delta G^o}{RT}\right] = \exp\left[\frac{nFE^o_{cell}}{RT}\right]$$

particular ion (e.g., hydrogen ion, H^+) is transported across the membrane. The transported ion will tend to move from the side with high concentration to the side with low concentration; however, in the process of doing so charge is separated across the membrane, producing a potential difference which exactly counters the ion transport. The membrane PD will be

$$\phi^{soln(rhs)} - \phi^{soln(lhs)} = \frac{RT}{z_jF} \ln \frac{a_j^{soln(lhs)}}{a_j^{soln(rhs)}} \approx \frac{RT}{z_jF} \ln \frac{c_j^{soln(lhs)}}{c_j^{soln(rhs)}} \tag{25}$$

where a_j and c_j are the activity and concentration of the transported ion. The cell emf is

$$E_{cell} = E_{re(rhs)} + \frac{RT}{z_jF} \ln \frac{c_j^{soln(lhs)}}{c_j^{soln(rhs)}} - E_{re(lhs)} \tag{26}$$

If the concentration on one side, e.g., $c_j^{soln(lhs)}$, is kept constant, E_{cell} will reflect any variation of the other concentration, $c_j^{soln(rhs)}$.

As long as the membrane transports only a single ionic species, the PD is thermodynamically determined. As soon as the membrane transports more than one ionic species irreversible thermodynamics come into play; the membrane PD will exhibit a complicated dependence on the concentrations and mobilities of the ions within the membrane as well as on their concentrations in the adjacent solutions. In certain circumstances, the response is still selective for one ion and the membrane electrode has analytical utility. The glass electrode used for measurement of pH, in which a thin glass membrane responds selectively to the H^+ ion, is an electrode of this type.

Potential differences called liquid junction potentials arise where two different ionic solutions make contact through a permeable separator such as a glass frit. These interfere with thermodynamic measurements and can be minimized by interposing a 'salt bridge', i.e., a concentrated immobilized solution of KCl, or other salt in which the cation and anion have nearly identical mobilities, between the two solutions. Numerous theories based on irreversible thermodynamics have evolved to estimate the magnitude of liquid junction potentials.

{*see* ION SELECTIVE MEMBRANES AND ELECTRODES; BIOPOTENTIALS}

What emf can do.

The emf produced by a single cell or a set of cells in series (a battery) is used as a DC power source for a wide array of applications requiring DC electric power, ranging from powering wrist watches to emergency power supplies. The emf of the saturated Weston cell

$$\mathrm{Hg}\,|\,\mathrm{Hg_2SO_4}\,|\,\mathrm{CdSO_4}\,(\text{saturated aq soln})\,|\,\mathrm{Cd\,(Hg)}$$

still serves as a high-level voltage reference for the National Institute of Standards and Technology; however, Josephson arrays are now considered the most precise voltage references and Zener diodes are used to produce reference voltages for many laboratory and field voltage measurement devices.

There are also a few photoelectrochemical cells with possible application in solar energy conversion, such as the Grätzel cell,

$$\mathrm{TiO_2(s)}\,|\,\text{adsorbed }\mathrm{Ru^{2+}}\text{ dye}\,|\,\mathrm{I_2, I^-}\,(\text{non-aq soln})\,|\,\mathrm{C}$$

where the cell emf is produced by absorption of visible light.

The emf of a cell can also be used as an indicator of chemical composition. Devices which depend on the measurement of an open circuit-cell potential work well when the device is sensitive to a single analyte but are notoriously sensitive to interferences (a familiar example is the 'alkaline error' which occurs when glass electrodes are used to measure very high pH values). For complex systems containing several species which can undergo electrochemical reaction, individual E° values can be determined using electroanalytical techniques which involve controlling the potential applied to a cell with measurement of the resultant current. Techniques such as polarography and cyclic voltammetry, for example, involve changing the potential of an indicator electrode and observing a wave or peak in the current at the redox potential of the species in solution; the height of the wave or peak indicates the concentration of the redox species present in the solution.

{*see* ELECTROCHEMISTRY; ELECTROCHEMICAL TECHNIQUES; POLAROGRAPHIC ANALYSIS; BATTERY; FUEL CELLS}

Cell voltages when current passes.

E_{cell} values, which are thermodynamic quantities, do not give any information about the kinetics of the electrode reactions. When current passes through a cell, the cell voltage (i.e., the sum of the PD's between the terminals) will differ from the emf because of resistive losses within the cell (a function of cell design) and because the kinetics of the electrode reactions are not fast enough to sustain thermodynamic (Nernstian) behavior at high rates of reaction (these kinetics are very dependent on temperature and the nature of the electrode material). When a cell is discharged through an external load, the cell voltage will be less than the emf; if the direction of current flow is reversed (using an external power supply) the cell voltage will be greater than the emf. In both cases, the greater the current, the greater the deviation of the cell voltage from the emf. In some cases the electrode reactions are so slow that even the open-circuit cell voltage may not be a reliable measure of the emf. For example, a cell comprising the two half cells, $2H^+(aq) + 2e^- \rightleftarrows H_2(g)$ and $O_2(g) + 4H^+(aq) + 4e^- \rightleftarrows 2H_2O$, both under standard conditions, has a cell emf of 1.223V at 25 C (see Table 1). A highly sophisticated version of this cell, the hydrogen/oxygen *fuel cell*, is designed to minimize internal cell resistance and has electrodes tailored to maximize the rates of the electrode reactions; nevertheless, the voltage under load is usually less than 0.8 V with most of the voltage loss occurring at the oxygen electrode.

When an external power supply is used to electrolyze water the cell voltage required to produce H_2 and O_2 at a reasonable rate is $\gtrsim 1.6$ V and this again depends critically on the cell design and the choice of electrodes.

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Table 1 Selected Standard Electrode Potentials at 25 C

Electrode	Electrode reaction	$E°$/V
$Li^+\|Li$	$Li^+(aq) + e^- \rightleftarrows Li(s)$	–3.045
$Zn^{2+}\|Zn$	$Zn^{2+}(aq) + 2e^- \rightleftarrows Zn(s)$	–0.763
$H_2\|H^+\|Pt$	$2H^+(aq) + 2e^- \rightleftarrows H_2(g)$	0
$Cl^-\|Hg_2Cl_2\|Hg$	$Hg_2Cl_2(s) + 2e^- \rightleftarrows 2Hg(s) + 2Cl^-$ (sat. KCl)	0.246
$Cl^-\|AgCl\|Ag$	$AgCl(s) + e^- \rightleftarrows Ag(s) + Cl^-(aq)$	0.222
$Cu^{2+}\|Cu$	$Cu^{2+}(aq) + 2e^- \rightleftarrows Cu(s)$	0.337
$Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}\|Pt$	$Fe(CN)_6^{3-}(aq) + e^- \rightleftarrows Fe(CN)_6^{4-}(aq)$	0.69
$O_2\|H^+\|Pt$	$O_2(g) + 4H^+(aq) + 4e^- \rightleftarrows 2H_2O$	1.223
$F_2\|F^-$	$F_2(g) + 2H^+ + 2e^- \rightleftarrows 2HF(aq)$	3.06

{For more complete Tables see: *Standard Electrode Potentials in Aqueous Solution*, ed. A J Bard, R. Parsons and J. Jordan, Marcel Dekker Inc., New York, 1985; *Tables of Standard Electrode Potentials*, G. Milazzo and S. Caroli, John Wiley & Sons, Chichester, 1978; *The Encylcopedia of Chemical Electrode Potentials*, M. S. Antelmann and F. J. Harris, Plenum Press, New York, 1982.}

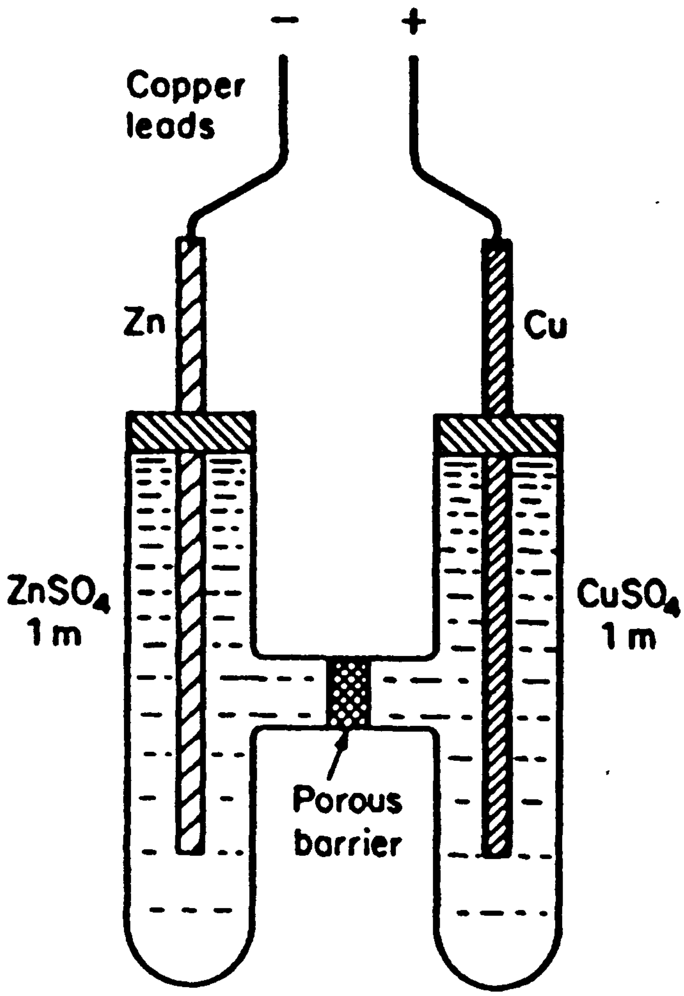

Figure 1: The Daniell cell (reproduced from W. J. Moore, *Physical Chemistry, 5th Edition*, Prentice-Hall, Inc., Englewood Cliffs, NJ, 1972; p. 524) - permission needed!